THERMAL ANALYSIS OF POLYMER SAMPLES BY A ROUND ROBIN METHOD. PART V. THERMOGRAVIMETRY

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ABSTRACT

The results of a round robin TG test are described. Decomposition temperature range and mass loss were measured for samples of polyethylene, epoxide resin, poly(ether sulfone) and polyacetal. The reproducibilities of these measurements are discussed in relation to the temperature reproducibility observed for the Curie temperatures of ICTA-NBS Certified Reference Materials and high-purity nickel wire.

INTRODUCTION

With the advancement of thermal analysis applications in polymer chemistry since the sixties, various techniques have been applied in research and development and then in production and trade. A need has arisen for the establishment of industrial standardizations of these techniques [1]. To achieve this, round robin DSC, DTA and TG tests have been carried out, and the Japanese Industrial Standards on these techniques for plastic materials (JIS K-7120-1987 through 7123-1987) are based on the results of these tests.

The DSC and DTA results for measurements of transition temperature, transition heat and heat capacity have been reported in a series of papers [2–5]. The present work is the final paper of this series, and describes the

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round robin test results for TG of plastic materials and standard materials. The round robin test was performed in 1986, and 11 organizations (6 private companies, 1 university and 4 public institutions) participated, as described in the first paper of the series [2] *. Decomposition temperature ranges, mass loss percentages and residues were determined.

A round robin test of TMA for the determination of softening temperatures of plastics, such as high temperature engineering plastics, was subsequently performed [6], and a similar round robin test of thermodilatometry of plastic materials is currently underway. The results will be used in the formulation of Japanese Industrial Standards on these two techniques.

EXPERIMENTAL

Samples

To examine reproducibility in temperature measurement, the tests used ICTA-NBS Certified Reference Materials (CRM) GM-761, and 1 mm diameter nickel wire of 99.997% purity, manufactured by Koch Chemicals Ltd.

The polymer samples used were: polyethylene film, as a typical example of a general purpose plastic material; two varieties of epoxide resin containing filter and glass fiber for residue measurement; poly(ether sulfonate), as a

TABLE 1

Polymer samples and atmosphere for TG

Sample	Specification	Atmosphere [a]
Polyethylene	Yukalon EY-40L Inflation film	Inert gas
Epoxide resin A	Cresol-novolak type Shaped article with filler	Air
Epoxide resin B	Cresol-novolak type Shaped article with filler and glass fiber	Air
Poly(ether sulfone)	Pellet	Inert gas
Polyacetal A [b]	Pellet	Inert gas
Polyacetal B [b]	Pellet	Inert gas

[a] Nitrogen or argon was used as the inert gas.
[b] Polyacetal A and B were samples of the same product, but of different grade.

* The name Suzuki in Table 1 of ref. 2 should have been given as S. Suzuki.

TABLE 2

Participants and apparatus

Participant	Apparatus	
	Manufacturer [a]	Type
A	Seiko	TG–DTA 200 SSC 5000
B	Shimadzu	TGA–40M
C	Rigaku	TG–DTA
D	Rigaku	TG–DSC
G	Shinku	TG–DTA
K	Shinku	TGD–7000 RH
L	Shimadzu	TG–30M
M	Rigaku	TG 8111 BS
N	du Pont	951 TGA
O	Rigaku	TG–DSC

[a] The full names of the makers are: Seiko Electronics Industries Co. Ltd., Shimadzu Corporation, Rigaku Corporation, Ulvac Sinku Riko CO. Ltd., and du Pont de Nemours and Co.

typical example of a high temperature engineering plastic; and two different grades of polyacetal, as examples of a polymer which undergoes some decomposition during fabrication. The specifications of these samples are given in Table 1.

Apparatus

The thermobalances used in this round robin test are listed in Table 2. Participants are represented by the symbols A–O.

Procedure

The procedure followed was essentially the same as that defined in ISO 7111-1987. The specimens of standard materials were in the form of cut sheets or cut wires, and the polymer specimens were used in 10 mg finely cut samples. The heating rate was 10 K min^{-1}. Air was used for most of the tests on the epoxide resins, at a flow rate of 50–100 ml min^{-1}. However, nitrogen was used by some participants. Nitrogen or argon was used for the other samples, at the same rate of flow.

RESULTS AND DISCUSSION

Temperature standards

In order to examine the reproducibility of the temperature measurements, observations were made of the apparent abrupt mass change at the Curie

TABLE 3

Temperature reproducibility observed with ICTA-NBS CRM GM-761 and pure nickel wire

Parameter	Permanorm 3			Nickel plate		
	T_1 (K)	T_2 (K)	T_3 (K)	T_1 (K)	T_2 (K)	T_3 (K)
$\bar{x}$	511.5	523.6	535.2	630.2	631.6	633.4
σ_n [a]	3.9 (0.8%)	3.6 (0.7%)	4.0 (0.7%)	5.0 (0.8%)	5.7 (0.9%)	5.3 (0.8%)
x_{max}	520	531	542	641	644	645
x_{min}	508	520.8	530	626	626	629
$x_{max} - x_{min}$	12	10.2	12.0	15.0	18.0	16.0

Parameter	Nickel wire			Mumetal		
	T_1 (K)	T_2 (K)	T_3 (K)	T_1 (K)	T_2 (K)	T_3 (K)
$\bar{x}$	630.7	631.9	633.5	653.5	663.8	674.4
σ_n [a]	4.2 (0.7%)	4.7 (0.7%)	5.4 (0.9%)	3.9 (0.6%)	4.8 (0.7%)	7.6 (1.1%)
x_{max}	640	642	645	661.1	669.3	681
x_{min}	627	627	628	650	654	658
$x_{max} - x_{min}$	13.0	15.0	17.0	11.1	15.3	23.0

Parameter	Permanorm 5			Trafoperm		
	T_1 (K)	T_2 (K)	T_3 (K)	T_1 (K)	T_2 (K)	T_3 (K)
$\bar{x}$	699.6	708.8	718.9	1017.6	1019.7	1021.2
σ_n [a]	7.5 (1.1%)	5.1 (0.7%)	4.7 (0.7%)	4.8 (0.5%)	4.0 (0.4%)	3.5 (0.3%)
x_{max}	710.2	715.0	727.8	1024	1026	1027
x_{min}	691	703	715	1010.6	1015.2	1018.2
$x_{max} - x_{min}$	19.2	12.0	12.8	13.4	10.8	8.8

[a] $\sigma_n = [\Sigma(xi - x)^2/n]^{1/2}$.

temperature of the ferromagnetic specimen under a magnetic field. The measurements were first made according to the instructions given in the certificate of ICTA-NBS CRM GM-761. However, many participants were not able to observe the apparent mass change, so the following procedure was recommended. The specimen was set in the thermobalance, and a permanent magnet or an electromagnet was advanced towards the thermobalance under operation until a sufficiently large apparent mass change was observed. Then the heating run was begun.

The results are shown in Table 3 and Fig. 1. In accordance with the procedure described in the certificate, readings were taken of the initial temperature T_1, the mid-point temperature T_2 and the end temperature T_3. Table 3 gives the means $\bar{x}$, standard deviations σ_n, maxima x_{max}, minima x_{min} and ranges ($x_{max} - x_{min}$). The scattering of the data can be seen in Fig. 1, where the temperatures obtained are plotted for each participant.

As can clearly be seen, the scattering for the nickel plate of the CRM and the high-purity nickel wire was small except in the case of participant L. In the experiment performed by participant L, the thermocouple junction in
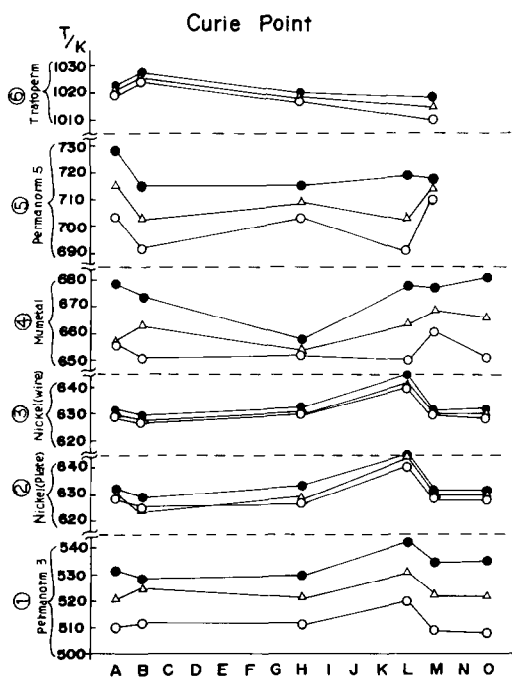
Fig. 1. Temperature: T_1 (○), T_2 (△) and T_3 (●) at Curie temperature are plotted for each participant (A–O).

the thermobalance was moved to the side of the sample container. When the junction was removed to the normal position beneath the container, the observed temperatures were close to the average and the scattering became much smaller. It is clear that pure nickel, either the CRM nickel plate or the easily available wire, is excellent for the purpose. When standard materials in the high temperature range are needed, Trafoperm is also very good.

Participants D, G and N did not succeed in observing the apparent mass change, though they were using different thermobalances. It is therefore to be recommended that the strong interaction between the specimen in the thermobalance and the outside magnet be confirmed before heating by observing the mass change as the magnet approaches. A strong magnet which does not disturb TG is also recommended.

Polymers

In the analysis of TG data on plastic materials, the following parameters are recommended (ISO 7111-1987, and also JIS K-7120 1987) for characterization of the materials. The mass gain m_G is given by

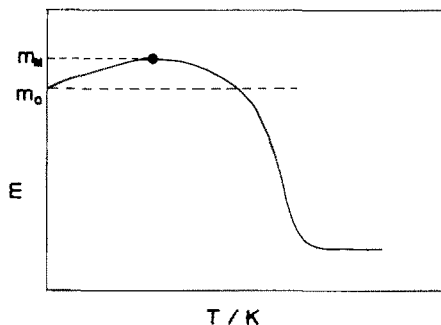$$m_G = \frac{m_M - m_0}{m_0} \times 100 \; (\%) \tag{1}$$

Fig. 2. Method for estimating mass gain from TG curve.

where m_0 and m_M are, respectively, the initial mass and the maximum, as shown in Fig. 2. Similarly, the mass loss m_L is given by

$$m_L = \frac{m_B - m_A}{m_0} \times 100 \ (\%) \tag{2}$$

where m_B and m_A are, respectively, the masses before and after thermal decomposition. For multiple-step decomposition, m_L is estimated for each step, as shown in Fig. 3. The residue R is the percentage ratio of the mass after the final decomposition to the initial mass.

The decomposition temperatures, i.e the initial temperature of decomposition T_1, the mid-point temperature of decomposition T_2 and the final temperature of decomposition T_3, can be estimated by the method presented in Fig. 4. Thus, the initial temperature of decomposition is the temperature corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve. The mid-point temperature of decomposition is the temperature corresponding to the mid-point of the step on the mass loss curve. The final temperature of decomposition is the temperature corresponding to the
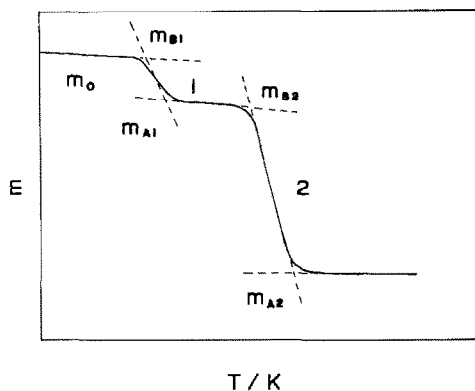

Fig. 3. Method for estimating mass losses of multiple-step decomposition from TG curve.
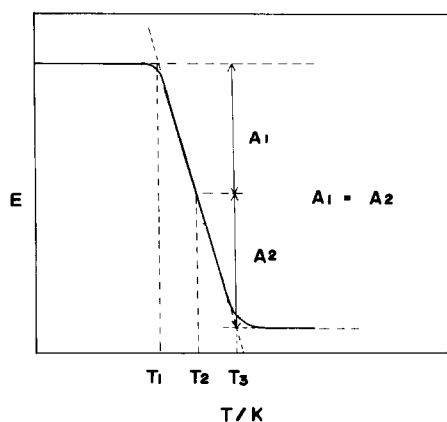
Fig. 4. Method for estimating decomposition temperatures from TG curve.

TABLE 4

TG data analysis for polyethylene

Group	Parameter	Mass loss m_L (%)	Decomposition temperature			Notes
			T_1 (K)	T_2 (K)	T_3 (K)	
A	$\bar{x}$	99.5	720.8	746.4	763.6	
	σ_n	1.0 (1.0%)	24.4 (3.3%)	8.9 (1.1%)	7.0 (0.9%)	
	x_{max}	100.0	740	758	778	
	x_{min}	96.7	653	724.4	749.7	
	$x_{max} - x_{min}$	3.3	87	33.6	28.3	($n = 11$)
B	$\bar{x}$	99.7	731.3	747.6	763.6	D and N excluded
	σ_n	0.5 (0.5%)	5.5 (0.8%)	4.9 (0.6%)	3.9 (0.5%)	
	x_{max}	100	740	758	773	
	x_{min}	98.3	722	740.1	759.4	
	$x_{max} - x_{min}$	1.7	18	17.9	13.6	($n = 9$)

TABLE 5

TG data analysis for epoxide resin A

Group	Parameter	Mass loss m_L (%)	Decomposition temperature			Notes
			T_1 (K)	T_2 (K)	T_3 (K)	
A	$\bar{x}$	27.0	643.0		835.1	A and N excluded
	σ_n	1.6 (5.9%)	40.9 (6.3%)		24.4 (2.8%)	
	x_{max}	29.0	733		858	
	x_{min}	23.3	597		785	
	$x_{max} - x_{min}$	5.7	136		73	($n = 9$)
B	$\bar{x}$	26.7	640.3	765.6	827.4	A, N, C, G
	σ_n	1.8 (6.7%)	50.0 (7.8%)	29.0 (3.8%)	26.4 (3.2%)	and O excluded
	x_{max}	27.9	733.2	801.0	858.0	
	x_{min}	23.3	597.0	718.0	785.0	
	$x_{max} - x_{min}$	4.6	136.2	83.0	73.0	($n = 6$)

TABLE 6

TG data analysis for epoxide resin B

Group	Parameter	Mass loss m_L (%)	Decomposition temperature			Notes
			T_1 (K)	T_2 (K)	T_3 (K)	
A	$\bar{x}$	34.2	636.1		880	A and N excluded
	σ_n	2.2 (6.4%)	54.4 (8.5%)		29.9 (3.4%)	
	x_{max}	39	711		918	
	x_{min}	31.4	539		813	
	$x_{max} - x_{min}$	7.6	172		105	($n = 9$)
B	$\bar{x}$	33.6	623.9	768.5	875.8	A, N, C, G and O excluded
	σ_n	1.6 (4.7%)	63.1 (10.1%)	22.7 (3.0%)	34.1 (3.9%)	
	x_{max}	36.7	711.0	788.0	918.0	
	x_{min}	31.4	539.0	720.0	813.0	
	$x_{max} - x_{min}$	5.3	172.0	68.0	105.0	($n = 6$)

intersection of the extended quasi-horizontal line after the decomposition step with the tangent at the inflection point. The values obtained for these temperatures are listed in Tables 4–9. The scattering of the data is shown in Figs. 5–8 for all the samples except the epoxides, which show either one-step or two-step mass loss, as described below.

The reproducibility of the mass loss measurements depends on the characteristics of the materials. The mass losses for polyethylene and poly-acetal sample B were over 99.5%. The standard deviations were about 1%, and the agreement was good. The data obtained by two of the participants, D and N, were scattered. In the run by D, the air purge seems to have been insufficient, and in the case of N, the temperature data were very inconsistent. If these two sets of data are excluded, the two standard deviations

TABLE 7

TG data analysis for poly(ether sulfone)

Group	Parameter	Mass loss m_L (%)	Decomposition temperature			Notes
			T_1 (K)	T_2 (K)	T_3 (K)	
A	$\bar{x}$	64.0	788.6	830.5	893.9	
	σ_n	12.0 (18.7%)	21.0 (2.6%)	20.9 (2.5%)	78.3 (8.7%)	
	x_{max}	99.5	817.7	886.2	1089.0	
	x_{min}	48.3	738.0	809.0	834.0	
	$x_{max} - x_{min}$	51.2	79.7	77.2	255.0	($n = 11$)
B	$\bar{x}$	58.6	791.0	822.3	876.7	D and N excluded
	σ_n	5.9 (10.0%)	12.5 (1.5%)	9.4 (1.1%)	75 (8.6%)	
	x_{max}	66.0	815.0	836.0	1089.0	
	x_{min}	48.3	775.0	809.0	834.0	
	$x_{max} - x_{min}$	17.7	40.0	27.0	255.0	($n = 9$)

TABLE 8

TG data analysis for polyacetal A

Group	Parameter	Mass loss m_L (%)	Decomposition temperature			Notes
			T_1 (K)	T_2 (K)	T_3 (K)	
A	$\bar{x}$	98.9	597.8	628.7	661.8	
	σ_n	1.9 (1.9%)	26.5 (4.4%)	11.8 (1.8%)	32.6 (4.9%)	
	x_{max}	100.0	694.4	724.4	758.0	
	x_{min}	94.1	523.0	614.0	638.0	
	$x_{max} - x_{min}$	5.9	171.4	110.4	12.0	($n = 11$)
B	$\bar{x}$	99.1	606.5	628.6	652.4	D and N excluded
	σ_n	1.9 (1.9%)	12.5 (2.0%)	12.9 (2.1%)	13.0 (2.0%)	
	x_{max}	100.0	627.0	652.0	675.0	
	x_{min}	94.1	589.0	614.0	638.0	
	$x_{max} - x_{min}$	5.9	38.0	38.0	37.0	($n = 9$)

TABLE 9

TG data analysis for polyacetal B

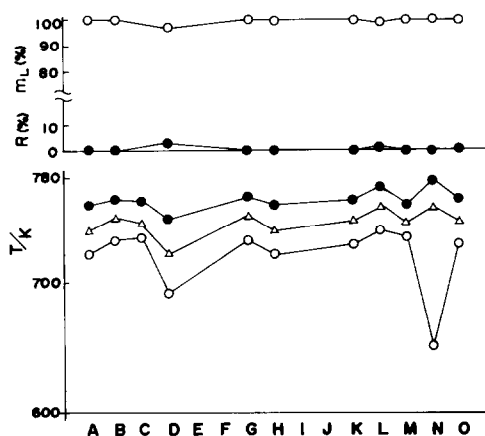| Group	Parameter	Mass loss m_L (%)	Decomposition temperature			Notes
			T_1 (K)	T_2 (K)	T_3 (K)	
A	$\bar{x}$	99.6	602.5	631.5	662.5	
	σ_n	0.9 (0.9%)	24.3 (4.0%)	17.2 (2.7%)	26.5 (4.0%)	
	x_{max}	100.7	629.0	654.0	718.0	
	x_{min}	97.0	538.0	606.0	624.0	
	$x_{max} - x_{min}$	3.7	91.0	48.0	94.0	($n = 11$)
B	$\bar{x}$	99.9	610.1	630.7	657.9	D and N excluded
	σ_n	0.35 (0.4%)	14.2 (2.3%)	17.9 (2.8%)	21.7 (3.2%)	
	x_{max}	100.7	629.0	654.0	683.0	
	x_{min}	99.5	590.0	606.0	624.0	
	$x_{max} - x_{min}$	1.2	39.0	48.0	59.0	($n = 9$)

Fig. 5. TG data for polyethylene: T_1 (○), T_2 (△), T_3 (●), m_L (○) and R (●) are plotted for each participant.
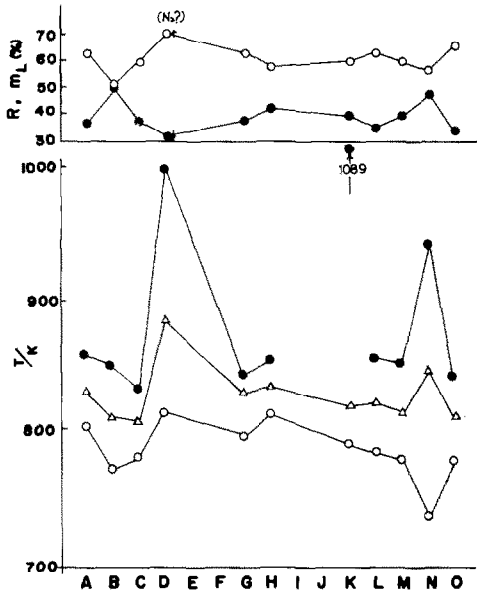
Fig. 6. TG data for poly(ether sulfone): T_1 (O), T_2 (Δ), T_3 (●), m_L (O) and R (●) are plotted for each participant.

are both about 0.5% and the agreement is very good. There seems to be an intrinsic precision of the TG analysis of polymeric materials, provided operating problems do not arise, e.g. with sample packing, or the nature of the sample.
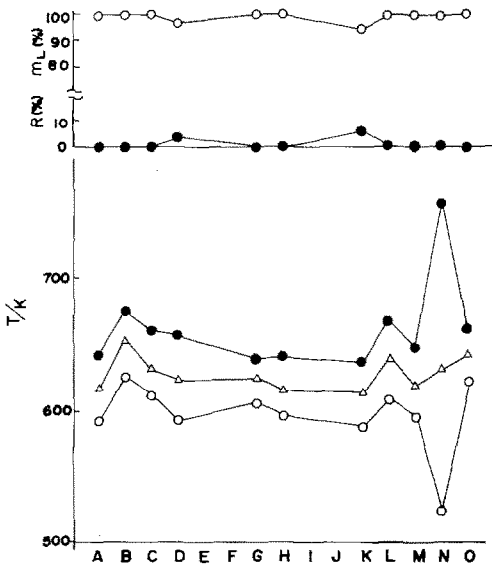

Fig. 7. TG data for polyacetal A: T_1 (O), T_2 (Δ), T_3 (●), m_L (O) and R (●) are plotted for each participant.
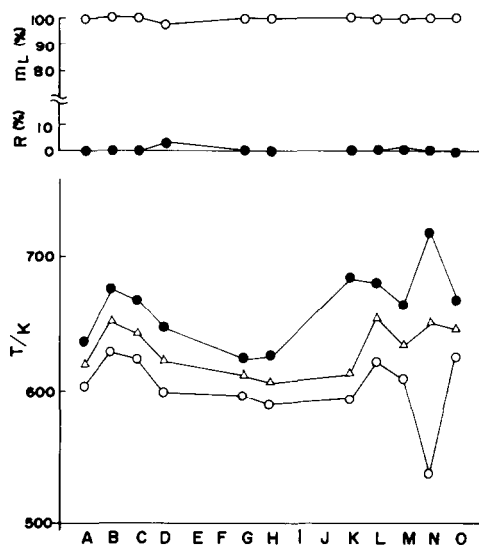
Fig. 8. TG data for polyacetal B: T_1 (○), T_2 (△), T_3 (●), m_L (○) and R (●) are plotted for each participant.

The standard deviation for polyacetal sample A was about 2%, the next closest result to the 0.5% values described above. The standard deviations for epoxide resin samples A and B were about 2% if the data obtained by A and N, who performed the TG in atmospheres other than air, are excluded. The scattering was greatest for poly(ether sulfone). The standard deviation for poly(ether sulfone) was 12%, or about 6% if the data obtained by D and N are excluded. In TG analysis of this material, the decomposition proceeds gradually within the wide temperature range above 1070 K, and the final temperature is also scattered, as described below. The inconsistency of the data obtained by D seems to have been caused by insufficient exchange of the atmosphere by nitrogen. Clearly, control of the atmosphere is also very important if good reproducibility is to be maintained. A similar tendency can also be pointed out for the residue, because addition of the values of m_L and R gives values of approximately 100% for all the samples.

The results of decomposition temperature measurement also depend on the characteristics of the sample. The B group of results in the tables does not include data obtained in the insufficiently exchanged atmosphere or in atmospheres other than those defined in the manual. The B group results are discussed below.

The values of T_1, T_2 and T_3 for polyethylene were in closest agreement; the standard deviations were less than 6 K, and those of the ranges were less than 18 K. For the epoxide resins the standard deviations were 23–70 K and the scatterings were fairly pronounced. Some participants observed one-step decomposition, while others obtained TG curves of two-step mass loss.
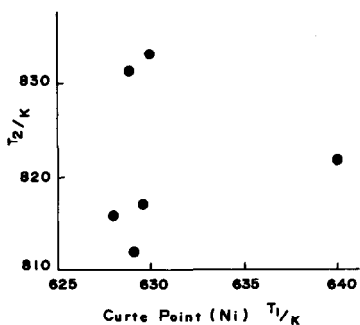
Fig. 9. Correlation between Curie temperature (abscissa) and mid-point decomposition temperature of poly(ether sulfone) (ordinate).

Procedural differences, involving e.g. fragmentation of the sample, may therefore be the cause of the large standard deviations.

For polyacetals A and B, as well as poly(ether sulfone), the standard deviations of T_1 and T_2 were within the range 9–23 K and the agreement was fairly good. However, the values of T_3 for poly(ether sulfone) were greatly scattered, as can be seen in Fig. 6. This was presumably due to gradual mass loss up to the high temperature range. The maximum value of T_3 was that observed by K (1089 K). Apart from this result, the scattering was fairly limited.

Correlation between Curie temperature and decomposition temperature

One example of this correlation is shown in Fig. 9, where the values of T_2 for poly(ether sulfone) are plotted against T_1 for the Curie temperature of nickel. As can be seen, no clear tendency emerges; this observation is also confirmed by statistical analysis, though the reproducibility of T_2 is fairly good. Similar results were obtained for the other samples. There was also a general tendency for the scatterings of the decomposition temperature for polymeric samples to be larger than those for the Curie temperature. As is discussed above, considerable scattering can be caused by certain elements of the procedure, such as the sample packing, or by certain conditions, such as insufficient air purge. Attention to these points is important if good reproducibility in the results of TG analysis of polymeric materials is to be achieved.

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